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EVALUATION OF INDOOR AIR POLLUTANT SINKS FOR VAPOR PHASE ORGANIC COMPOUNDS

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The interaction of indoor air pollutants with interior surfaces (i.e., sinks) is a well known, but poorly understood, phenomenon. Studies have shown that re-emissions of adsorbed organic vapors can contribute to elevated concentrations in indoor environments. Research is being conducted in small environmental test chambers to develop data for predicting sink behavior. This paper reports on small chamber tests and on the development of sink models based on fundamental mass transfer theory.

INTRODUCTION

The interaction of indoor air pollutants with interior surfaces (i.e., sinks) is a well known phenomenon. Berglund *et al.* (1) presented an extensive review of the literature on adsorption and desorption of vapor phase organic compounds in indoor environments. The Danish Town Hall Study provided empirical evidence that re-emission of indoor pollutants, including vapor phase organics, from fleecy (i.e., large surface area) materials contributes to Sick Building Syndrome (2). Seifert and Schmahl (3) reported on research to determine the adsorption and desorption behavior of several organic compounds and several surface materials, but concluded "... no rule can be deduced to predict the sorption behavior of different VOC with different materials."

THEORY

Langmuir Isotherm

The Langmuir isotherm (4) assumes a monolayer of molecules on a homogeneous surface with all adsorption sites mutually independent and identical (i.e., all sites require the same energy to adsorb molecules). At low concentrations, the Langmuir isotherm can be represented by:

$$k_a C_e A = k_d M_e A \qquad [1]$$

where k_a is the adsorption rate constant; C_e is the equilibrium concentration in air; A is the sink area; k_d is the desorption rate constant; and M_e is the mass in the sink at equilibrium. Also, an equilibrium constant, k_e, can be defined as:

$$k_e = k_a/k_d = M_e/C_e \qquad [2]$$

Application to Chamber Testing

Dunn and Tichenor (5) proposed the following differential equation to describe the mass balance in a test chamber:

$$VdC/dt = dx/dt - dy/dt - dw/dt \quad [3]$$

where V is the chamber volume; C is the concentration in the chamber; dx/dt = R(t) is the rate of mass entering the chamber; dy/dt = NCV (N is the air exchange rate) is the rate of mass leaving the chamber; and dw/dt is rate of change of mass in the sink. The sink term can be expressed as:

$$AdM/dt = k_3CV - k_4MA \quad [4]$$

where M is the mass per unit area in the sink; k_3 is the rate constant to the sink; and k_4 is the rate constant from the sink.

If a Langmuir adsorption process is assumed, comparing equations [1] and [4] yields $k_3 = k_a(A/V)$ and $k_4 = k_d$. By substituting k_a and k_d in equation [3]:

$$VdC/dt = R(t) - NCV - k_aCA + k_dMA \quad [5]$$

Substituting L = A/V in equation [5] gives:

$$dC/dt = R(t)/V - NC - k_aCL + k_dML \quad [6]$$

Substituting k_a and k_d into equation [4] and dividing both sides by A gives:

$$dM/dt = k_aC - k_dM \quad [7]$$

Thus, if Langmuir adsorption processes are assumed, equations [6] and [7] describe the rate of change of concentration and sink mass, respectively, for small chamber tests.

EXPERIMENTAL METHODS

Experiments to determine adsorption and desorption rates for vapor phase organic compounds were conducted in small (53 liter) environmental test chambers (6).

Test Materials and Compounds

Five sink materials were evaluated: a) nylon carpet; b) painted wallboard; c) ceiling tile; d) window glass; and e) upholstery (throw pillow with polyester fiber fill). Each material was tested with two organic compounds commonly found in indoor air: tetrachloroethylene, a cleaning solvent; and ethylbenzene, a constituent of petroleum based solvents.

Test Procedures

A sample of the sink material was placed in a test chamber supplied with clean, humidified air at a nominal flow rate of 1 air change per hour (ACH). At the start of each test, a portion of the inlet flow was replaced by flow from a constant temperature oven that held a permeation tube containing the test compound. The test compound was added to the chamber inlet flow at a constant rate for 48 hours, then the flow from the permeation device was shut off and replaced by flow from the clean air system.

The concentration of the test compound was monitored at the outlet of the chamber by gas chromatography. Samples were collected as frequently as possible for the first few hours in order to define the rising portion of the concentration vs. time curve (see Figure 1). Once the concentration reached an apparent equilibrium value, the sampling frequency was decreased. Forty-eight hours after the start of the test, the injection of the organic compound was terminated. At this point, the sampling frequency was again increased. Sampling continued until the concentration reached the quantification limit of the method.

Test Conditions

A wide variety of test conditions were used. Initial testing was conducted on carpet with tetrachloroethylene to investigate the effect of concentration and temperature on the sorption behavior. Subsequent tests with the other materials and with ethylbenzene were conducted under fewer conditions. Tests to determine the sink behavior of empty chambers were also carried out. All tests were conducted at a nominal 1 ACH and a water vapor content equivalent to 45% relative humidity at 23°C.

DATA ANALYSIS

Data obtained from the small chamber tests were analyzed to yield estimates for M_e, k_a, k_d, and k_e. M_e was determined from the area under the C vs. t curve from t_s (see Figure 1) to the end of the test and subtracting the mass in the chamber at time t_s. Equations [6] and [7] were solved analytically and fitted to the chamber data using a non-linear, least squares curve fit computer program to obtain values of k_a and k_d.

RESULTS AND DISCUSSION

The crosshatched areas in Figure 1 clearly show the effect of adsorption to and desorption from the sink material, in this case, carpet. All the other test runs showed similar results, except for window glass and the empty chamber, which exhibited no measurable sink effect.

Applicability of Langmuir Isotherm

Figure 2 presents a plot of M_e vs C_e for tetrachloroethylene and carpet at 23°C. The plot shows a linear relationship with a slope of 0.97 and an r^2 correlation of 0.98. This linearity confirms the applicability of the Langmuir equilibrium at low concentrations represented by equation [1] [i.e., $M_e = (k_a/k_d)C_e$] and equation [2], with the slope of the line equal to the average k_e value for the 10 tests (see Table 1).

Fitting the kinetic data (i.e., C vs t) to obtain k_a and k_d values based on a Langmuir sorption process showed a "good fit" for ceiling tile and wallboard, but the fit of the data for the pillow and carpet data indicates that the desorption deviates from the Langmuir assumptions. Thus, it appears that Langmuir kinetics apply to relatively flat, smooth surfaces (e.g., ceiling tile, wallboard), but may be inappropriate for more complex surfaces (e.g., carpet and upholstery). In spite of the relatively poor fit of the kinetic data for carpet and pillow, it is felt that the values of k_a, k_d, and k_e for these materials can be used to compare their sorption behavior with other materials and to compare the sink effects of different compounds.

Langmuir Rate Constants

The experimental results (average values for k_a [m/hr], k_d, [1/hr] and k_e [m]) and the number of test runs (n) are presented in Table 1. Since the tests conducted on the empty chamber and on window glass showed no sink effect, no results are presented for these experiments. All tests were conducted at 23°C, except where noted.

Table 1: Average Adsorption and Desorption Rate Constants and Equilibrium Constants - Langmuir Isotherm Model

		Carpet	Carpet (@35°C)	Wallboard	Ceiling Tile	Pillow
Tetra-chloro-ethylene	k_a	0.129	0.304	0.212	0.100	0.026
	k_d	0.133	0.590	1.50	0.613	0.101
	k_e	0.970	0.516	0.142	0.163	0.254
	n	10	2	2	2	2
Ethyl-benzene	k_a	0.078	-----	0.449	0.240	0.004
	k_d	0.081	-----	1.50	0.588	0.016
	k_e	0.954	-----	0.301	0.409	0.273
	n	2	0	2	2	2

Sink Strength

The capability of a sink material to adsorb indoor air pollutants is represented by k_e; the higher the k_e value, the greater the mass adsorbed on the sink at a given concentration (i.e., the stronger the sink). An analysis of variance (AOV) of the k_e values showed a significant ($p = 0.055$) COMPOUND X MATERIAL interaction (i.e., the differences in the k_e values among the materials depend on the compounds). Carpet was a significantly stronger sink ($p < 0.01$) than the other three materials for both compounds, while no significant differences in k_e were detectable ($p = 0.01$) among the other three materials for either compound. However (see Table 1), there was an apparent difference in ordering of the sink strength: pillow > ceiling tile > wallboard for tetrachloroethylene; and ceiling tile > wallboard > pillow for ethylbenzene. As stated previously, glass was not a sink for either compound.

The sink strength of the two compounds tested are also different. Ceiling tile adsorbed significantly more ($p = 0.005$) ethylbenzene than tetrachloroethylene. A similar trend ($p = 0.05$) was evident for wallboard. For carpet and pillow, no differences ($p = 0.79$ and $p = 0.80$, respectively) in sink strengths were observed between the two compounds.

Adsorption and Desorption Rates

Values for k_a and k_d were analyzed to determine differences in adsorption and desorption rates for the materials and compounds tested. An AOV indicated a significant MATERIAL X COMPOUND interaction for k_a ($p = 0.0016$), but not for k_d ($p = 0.99$). Other findings include:

- Wallboard and ceiling tile adsorbed ethylbenzene at significantly higher rates ($p < 0.01$) than carpet and pillow.

- Wallboard adsorbed tetrachloroethylene at significantly higher rates ($p < 0.01$) than the pillow, with carpet and ceiling tile representing intermediate, but indistinguishable, values.

- Ethylbenzene adsorbed at a significantly higher rate than tetrachloroethylene on wallboard ($p = 0.003$) and ceiling tile ($p = 0.015$). There were no significant differences in the adsorption rates for the two compounds for carpet ($p = 0.22$) and pillow ($p = 0.68$).

- Wallboard desorbed at a significantly higher rate ($p < 0.01$) than the other three materials. Ceiling tile desorbed at a significantly higher rate ($p < 0.01$) than carpet and pillow, which are indistinguishable.

- There was no significant difference ($p = 0.56$) in the desorption rates for ethylbenzene and tetrachloroethylene for any of the sink materials.

Effect of Temperature

Only limited data were collected to investigate the effect of temperature. Based on thermodynamics, both the adsorption and desorption rates should be higher at elevated temperatures. The values for k_a and k_d for the tetrachloroethylene/carpet tests conducted at 35°C indeed show significantly higher values than those observed at 23°C.

CONCLUSIONS

Experiments conducted to examine the behavior of indoor sinks vis-a-vis vapor phase organic compounds have clearly shown adsorption to and re-emission from common indoor materials for two typical indoor air pollutants. Of the five materials tested, only window glass had no sink effect. Both the type of material and the type of organic compound affect the rates of adsorption and desorption, as well as the equilibrium mass in the sink. Higher temperatures increase both the adsorption and desorption rates. Fundamental Langmuir adsorption theory appears adequate to describe the behavior of smooth materials, such as wallboard and ceiling tile. The desorption kinetics of rough, complex materials, such as carpet and upholstery, appear to be governed by non-Langmuir processes. Further research is needed to better understand and describe the behavior of indoor sinks.

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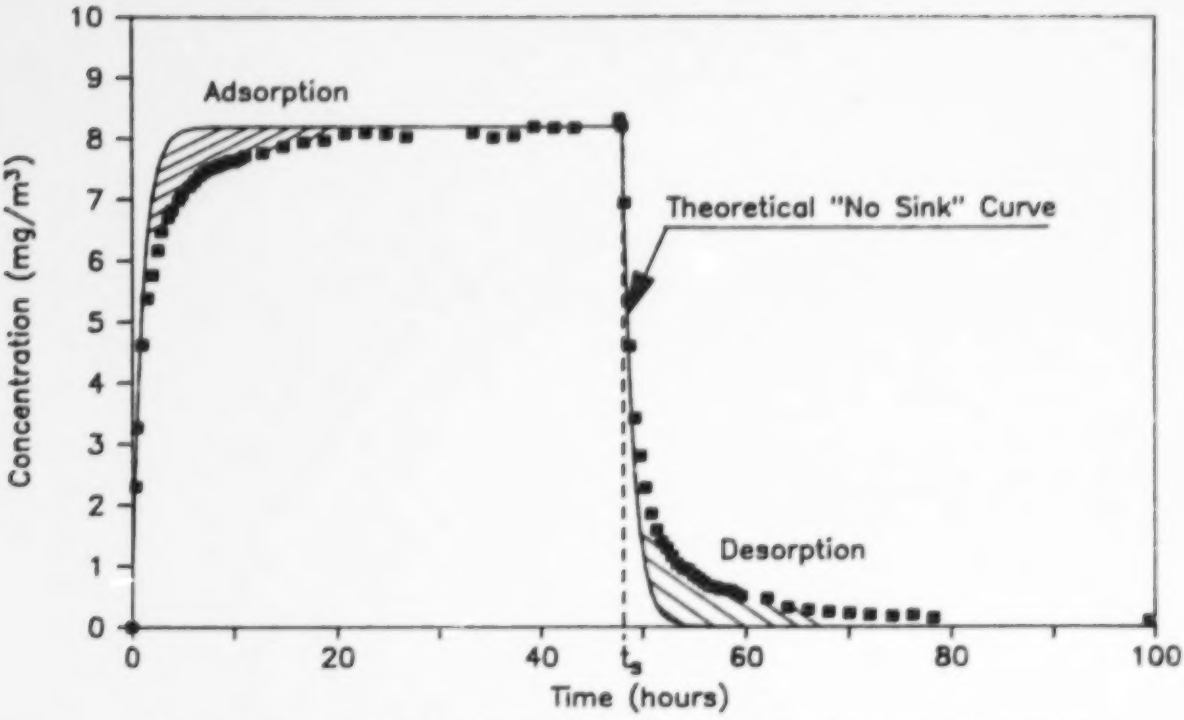

Figure 1 – Chamber Test: Ethylbenzene/Carpet

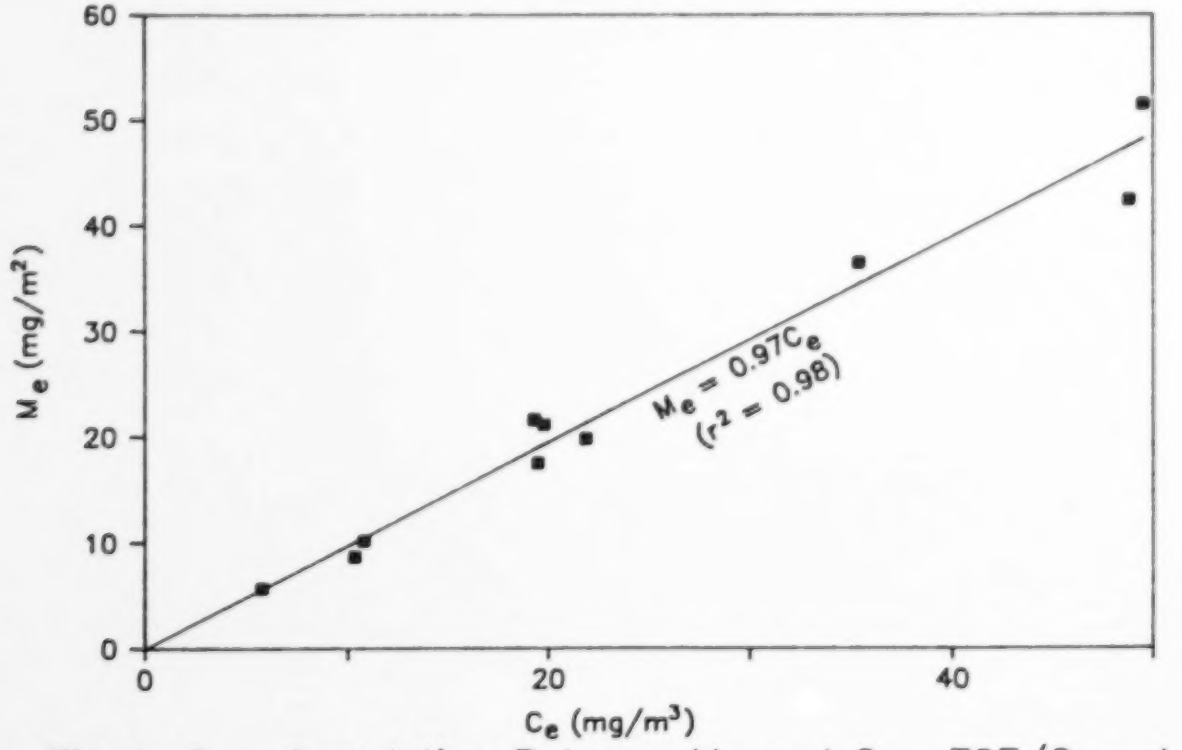

Figure 2 – Correlation Between M_e and C_e : TCE/Carpet